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(54) PHOTOGRAPHIC SILVER HALIDE COLOUR PROCESSING

(71) We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester, New York 14650, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the processing of imagewise exposed silver halide colour photographic film materials and to developer replenishers for use therein.

Photographic multilayer, silver halide, incorporated coupler, negative colour film materials are those films which on exposure to a subject (positive image) and processing are designed to result in a negative colour image which can be used as a negative from which photographic colour prints are made, or conversely on exposure to a negative are designed to form a positive transparency. The processing of such films involves subjecting the film to a series of processing steps which include: developing the film to simultaneously form silver images and dye images in the exposed areas; stopping the development with an acidic stop bath, hardening, bleaching the hardened film by converting developed silver to silver ions and fixing to remove silver ions from the film.

In continuous film processing methods which are designed to process large quantities of film over an extended period of time, the effectiveness of the developer is maintained by adding developer replenisher to the original solution. The replenisher must not only make-up for components used during processing and loss through carry-over, but also overflow loss by volume increase when the replenisher is added. The replenishment can be accomplished while the developer is in use by adding replenishment in continuous fashion or at periodic intervals, usually at a specified amount of replenisher for each square foot of film processed.

In such processes it has heretofore been considered necessary to use a developer replenishment rate of at least 325 ml. of developer replenisher per square foot of processed film (normally 485 ml. per square foot of picture area) to assure high-quality, reproducible development.

We have found that by using developer replenishers having high potassium/sodium ion weight ratio in such processes, high-quality development can be obtained at a replenishment rate which is one-half or even less of the rate previously considered necessary for satisfactory results. These surprisingly effective developer replenishers are advantageously prepared from replenisher kits having at least two solutions, one containing concentrated acidic developing agent solution and another containing a concentrated aqueous solution having a buffer controlled high pH.

According to the present invention there is provided a method of processing photographic multilayer, silver halide, incorporated coupler, negative colour films wherein a developer replenisher is employed which contains a p-phenylenediamine developing agent, benzyl alcohol and sulphite ions and has a pH of at least 10.5 at 24°C. characterised in that the developer replenisher contains potassium and sodium ions in a potassium/sodium ion weight ratio of at least 2.5/1.

The invention also provides a developer replenisher solution having a pH of at least 10.5 at 24°C. and containing potassium and Sodium ions, a *p*-phenylenediamine developing agent, benzyl alcohol and sulphite ions characterised in that potassium and sodium ions are present in a potassium/sodium ion weight ratio of at least 2.5/1.

The developer replenisher solution of the invention may be in the form of a concentrated

[*Price 25p*]

kit comprising at least two aqueous solutions one of which contains a buffered solution having a pH of at least 10.5 at 24°C. and containing sulphite, another solution containing the developing agent and having a pH of less than 6 at 24°C. which solutions when mixed together and with water provide developer replenisher solutions according to the invention.

In one embodiment of the present invention the buffered solution of the replenisher kit is a concentrated, buffered aqueous solution having a pH in excess of 10.5, advantageously above 10.75 at 24°C. (normally buffered solutions having a high pH decrease in pH with increase in temperature) and containing hydroxide ions, buffer, e.g., phosphate, carbonates or advantageously boric acid-borate buffer, and sodium and potassium ions so that the potassium/sodium ion weight ratio is at least 2.5/1, especially at least 5.4/1.0. This solution also contains some sulphite ions (e.g., supplied as sodium or potassium sulphite or bisulphite) and/or sequestering agent, such as ethylene-diamine tetraacetic acid and advantageously diaminopropanol tetraacetic acid. In some instances it is also desirable to have small amounts of bromide present in the buffered solution.

The buffered solution may be prepared in a number of ways but it is especially advantageous to add alkali metal hydroxides to water and then a weak acid to the alkaline solution to form the buffer. The alkali metal hydroxide/weak acid ratio used to form the buffer may vary to some degree but it is desirably about a 1/1 mole ratio and advantageously 1—1.1/1 to maintain the desired pH and buffer capacity. It is especially advantageous to use potassium hydroxide as the main source of hydroxide but some sodium hydroxide can be used with effectiveness.

The concentration of the ingredients in the buffered solution can vary considerably. However, the solutions are desirably concentrated so that shipping, packaging, and handling costs are reasonably low. However, the concentration should be sufficiently low so that no crystallization occurs since such crystals are often difficult to redissolve. Solutions having a cationic concentration of about 7—15 molar are generally desirable especially when the cations consist essentially of potassium and sodium in a potassium/sodium weight ratio of at least 2.5/1, advantageously 5.4/1.0 and especially 5.4 to 10/1.0.

The hydroxide and weak acid concentrations desirable in such a solution will be dictated by the pH and buffer capacity desired but usually the alkali metal hydroxides constitute the main source of alkali metal.

The sulphite concentration of such kit components is dictated by the amount of sulphite necessary in the replenisher. A concentration of 0.15 to 0.4 molar in the kit is usually desirable. Although, as mentioned above, it is sometimes desirable to have some bromide present, the bromide content of the fresh, ready-to-use replenisher is preferably no higher than 0.010 molar and advantageously no higher than 0.009 molar. Thus, if the bromide were added, for example, as sodium bromide, the total sodium bromide used would preferably be no greater than 1.0 gram for sufficient concentrate to make one litre of replenisher or no greater than 0.2 molar in the replenisher kit.

The buffered solution is advantageously one solution of a developer replenisher kit which includes at least another solution comprising *p*-phenylenediamine developing agent at high concentration in aqueous solution having a pH less than 6, advantageously less than 4. The *p*-phenylenediamine developing agents which are used in this solution are the colour developing agents well known in the art.

The concentration of the developing agent will, of course, vary depending, *inter alia*, upon the specific developing agent selected. For economic reasons, it is advantageous to have a highly concentrated solution, particularly between 1—6 grams developer (as free diamine) per 10 grams of water, for the replenisher kit component. When 4 - amino - N - ethyl - N - [β - methanesulphonamido - ethyl] - *m* - toluidine is used as the developing agent it is desirable to use a concentration of about 5 grams of the free diamine (i.e. about 7.8 grams of the sesquisulphate monohydrate) for each 10 grams water.

The developer replenisher according to the present invention contains sulphite. As mentioned above, sulphite is advantageously included in the buffered solution. It is also desirable to include sulphite in the developing agent solution desirably in a developing agent (as free amine)/sulphite mole ratio of from 1/0.08 to 1/1.5, especially from 1/0.15 to 1/0.5. (Mole ratios of diamine set forth herein relate to the moles of available diamine in the solution not necessarily moles of salt added, e.g., 846 grams of 4 - amino - N - ethyl - N - [β - methanesulphonamido - ethyl] - *m* - toluidine sesquisulphate monohydrate, is considered to include 2 moles of diamine).

Benzyl alcohol is included in the developer according to the present invention and it, too, is advantageously included in the developing agent solution desirably at a phenylenediamine/benzyl alcohol weight ratio of no less than 1/2 and especially between 1/1.5 and 1/2. A highly advantageous method of incorporating the benzyl alcohol in the concentrated developing agent solution is by utilizing a simple liquid glycol with a carbon/oxygen ratio of .75 to 1.5/1 and molecular weight of from 62 to 150, desirably in a benzyl alcohol/glycol weight ratio between

0.7/1 and 1/1. Particularly advantageous glycols are propylene glycol, diethylene glycol, and triethylene glycol, and especially ethylene glycol. With such compounds the benzyl alcohol can be combined with acidic aqueous solutions to form clear solutions in a high benzyl alcohol concentration, a water/benzyl alcohol weight ratio of from 1/6 to 5/1.

The developing agent solutions containing benzyl alcohol may be prepared by simply combining the various ingredients. However, to obtain maximum concentration and convenience and minimize the necessity for rechecking the component quantity accuracy, the solution is formed by first combining water with the desired amount of sulphite, and then dissolving the *p*-phenylenediamine developing agent (usually as the acid salt) in the sulphite solution. The benzyl alcohol is then added to form a cloudy slurry after which at least sufficient glycol is added to convert the slurry into a clear solution.

The developing agent solution of the developer replenisher kit preferably contains benzyl alcohol and some sulphite. The buffered solution may contain additional sulphite, accelerators and complexing agents, e.g., polyphosphates, sodium hexametaphosphates, nitrilo acetic acid, methylamino diacetic acid, dimethylethylene diamino diacetic acid, ethylenediamine tetraacetic acid, and diaminopropanol tetraacetic acid. The placing of addenda in other or separate containers may be desirable.

The developer replenisher kit may be converted into a developer replenisher by combining the developing agent solution and the buffered solution with water, desirably by first mixing the concentrated developing agent solution which may contain benzyl alcohol with a desired amount of water and subsequently adding the buffered solution and adjusting to final concentration by adding water.

The ready-to-use developer replenisher according to the present invention preferably has a pH of 10.5 to 11, desirably 10.6 to 10.9 at 24°C. The potassium/sodium ion weight ratio is in excess of 2.5/1, advantageously in excess of 4/1, and especially above 5.4/1. It is frequently advantageous to utilize a potassium/sodium ion weight ratio between 4/1 and 10/1 with ratios between 5.4/1 and 10/1 being especially preferred. In a preferred embodiment of the invention no cations other than sodium and potassium are present in the buffered solution.

The developing agents and concentrations used in the replenisher kit desirably result in a replenisher concentration of 3 grams to 5 grams per litre based on the weight of available free amine. In an especially desirable embodiment of the present invention 3.8 to 4.5 grams of 4 - amino - N - ethyl - N - [β - methanesulphonamidoethyl] - *m* - toluidine are utilized per litre of replenisher solution.

For highly effective replenishers according to the present invention, it is important that the benzyl alcohol in the ready-to-use replenisher be used at a concentration of no more than 8 grams per litre, normally from 4 to 8 grams per litre, desirably from 6 to 7.5 grams per litre. Similarly, if any bromide is utilized in the developer replenisher, it is important that no more than 0.80 gram bromide be used per litre of replenisher. Thus, if the bromide is supplied to the solution as sodium bromide, no more than 1.0 gram sodium bromide should be utilized per litre of replenisher.

The replenisher also contains sulphite desirably in concentration of 1.25 grams to 1.55 grams per litre of solution or in a total *p*-phenylenediamine/sulphite mole ratio of about 1/1.6. The sulphite is desirably supplied to the solution as an alkali metal sulphite or bisulphite, desirably as sodium sulphite.

An especially effective buffer system which may be used in the present invention is the boric acid-borate system, desirably supplied to the kit solution by incorporating therein the alkali metal hydroxides and 18 to 30 grams especially 25 to 30 grams boric acid per litre of replenisher solution to maintain the pH of the solution at the desired level. The resultant replenisher solution contains from 19 to 28.5 grams per litre borate in various states of dissociation, i.e., boric acid and/or the dissolved borate containing residues from the boric acid.

In a highly effective embodiment of the present invention the dissolved residues from diaminopropanol tetraacetic acid (sequestering agent) are also included in the replenisher especially at a concentration of from 1 to 1.5 grams per litre of solution.

The developer advantageously contains substantially the same ingredients as the developer replenisher described above. The same developing agent, for example, is desirably used in both the developer and replenisher. Similarly, benzyl alcohol, sulphite, and buffer are desirably utilized in the developer. However, according to the present invention, the concentrations of various ingredients in the developer vary considerably from those of the replenisher. Although the potassium-sodium ratio in the developer, for example, is desirably similar to that of the developer replenisher, the ratio in the developer is not very important.

To obtain optimum effectiveness it is very important that the concentration of benzyl alcohol in the replenisher be at least 0.2 gram per litre greater than the concentration of benzyl alcohol in the developer. In the developer, a benzyl alcohol concentration of from 3.8 to 7.8 grams per litre is suitable. A con-

centration of benzyl alcohol in the developer of from 5.6 to 6.0 grams per litre is especially effective while a concentration of from 6.2 to 7.2 grams per litre benzyl alcohol would be suitable for a corresponding replenisher solution.

It is also important to optimum effectiveness that the developing agent be present in a higher concentration in the replenisher than in the developer by at least 0.4 gram per litre based on the weight of available diamine especially when the replenisher contains 3 grams to 5 grams developing agent selected from 2 - amino - 5 - diethylaminotoluene; 4 - amino - N - ethyl - N - [β - methane - sulphonamidoethyl] - *m* - toluidine; 4 - amino - 3 - methyl - N - ethyl - N - [β - hydroxyethyl] - aniline; and 4 - amino - 3 - [β - methylsulphonamidoethyl] - N,N - diethylaniline. From 3.2 to 3.8 grams 4 - amino - N - ethyl - N - [β - methane - sulphonamidoethyl] - *m* - toluidine per litre is especially effective for the developer, while the corresponding concentration for a replenisher used with such a developer is from 3.9 to 4.5 grams 4 - amino - N - ethyl - N - [β - methanesulphonamidoethyl] - *m* - toluidine per litre.

It is extremely important to maximum effectiveness of the system that the bromide concentration of the replenisher be substantially lower than the concentration of bromide in the developer. For example, the developer bromide concentration is nearly always at least 1 gram per litre (corresponding to at least about 1.3 grams sodium bromide per litre) whereas for optimum effectiveness the replenisher bromide concentration, if any is present, should be no greater than 0.80 gram per litre (corresponding to 1 gram sodium bromide). In one advantageous embodiment of the present invention the bromide concentration is between 0.60 and 0.80 grams per litre.

Sulphite concentrations for the developer can vary somewhat but for maximum effectiveness should be between 1.2 grams (e.g., supplied as 1.9 grams sodium sulphite) to 1.5 grams per litre. The corresponding replenisher then would desirably contain slightly more than the developer, from 1.25 to 1.55 grams per litre. As with the replenisher, the sulphite is normally supplied to the solution as an alkali sulphite or bisulphite.

The developer also desirably contains a buffer system which is provided in a manner analogous to that for the replenisher except that the resultant pH is desirably slightly lower for the developer. Highly suitable buffer systems result from the dissolution of boric acid and alkali metal hydroxides so that the total borate concentration, including boric acid and/or dissociated residues thereof, is from 26.5 to 27.0 grams per litre. A replenisher for such a developer desirably would have a total borate concentration of from 27.2 to 27.8 grams per litre.

The developer also desirably contains sequestering agent, desirably the dissolved residues from 0.8 to 1.3 grams per litre of diamino propanol tetraacetic acid. With such a developer, a replenisher having the same sequestering agent in a concentration of from 1.0 to 1.5 grams per litre would advantageously be utilized. In general, the replenisher solution may contain from 0.5 to 2.0 grams sequestering agent per litre of solution.

The following Examples illustrate the invention.

Example 1

A three-component developer replenisher kit is prepared containing Parts A, B, and C as follows:

Part A

About 6.3 ml. benzyl alcohol.

Part B

A concentrated buffer solution is prepared by dissolving 3.4 grams NaOH and 22.8 grams KOH in 63 grams water; then, slowly adding about 29 grams boric acid; and adjusting the pH of the resultant solution to 10.75 at 27°C. by the addition of small amounts of potassium hydroxide (45% solution).

Part C

A concentrated acidic solution containing developing agent is prepared by dissolving 2 grams sodium sulphite in 11 grams water, and adding 6.4 grams 4 - amino - N - ethyl - N - [β - methanesulphonamidoethyl] - *m* - toluidine sesquisulphate monohydrate with stirring.

Example 2

A photographic developer replenisher is prepared by adding the 6.2 grams benzyl alcohol (Part A, Example 1) with vigorous stirring to about 800 ml. water; adding to the resultant solution with stirring the solution from Part B (Example); after Part B is fully dissolved, adding Part C (Example 1) with stirring and adding water to adjust the volume to one litre at 27°C.

Example 3

The solution from Example 2 is then utilized as a developer replenisher in processing an imagewise exposed commercially available silver halide colour negative film material having respectively superposed on and adhered to a transparent support a red sensitized gelatinous emulsion layer containing non-diffusing cyan dye-forming coupler, a green sensitized gelatinous emulsion layer containing non-diffusing magenta dye-forming coupler, a yellow filter layer, and a blue

sensitized emulsion layer containing non-diffusing yellow dye-forming coupler. The developer which is replenished contains the dissolved residues from approximately 5.8 grams benzyl alcohol, 28.1 grams boric acid, 5.4 grams 4 - amino - N - ethyl - N - [β - methanesulphonamidoethyl] - m - toluidine sesquisulphate monohydrate, 1.9 grams sodium sulphite, 3.2 sodium hydroxide, 20.5 grams of potassium hydroxide, and 1.5 grams sodium bromide per litre of solution.

The process involves developing the film as described above for a period of about 14 minutes at about 24±0.03°C., and the following steps in the order indicated at 24±1°C: stopping the development by treating the developed film in an acetic acid stop bath for 4 minutes; treating the film in a gelatin hardener solution containing formaldehyde and methanol for 4 minutes; washing the film in running water for 4 minutes; treating the film in a bleach bath containing ferricyanide and bromide for 6 minutes; washing the film in running water for 4 minutes; treating the film in a hypo fix bath for 8 minutes; washing the fixed film for 8 minutes; and then drying the film at about 32°C.

The developer replenisher functions effectively when added to the developer at a rate of 243 ml. per square foot of picture area produced (163 ml. per square foot of film processed).

Example 4

The procedure according to Example 3 is followed except that the developer replenisher contains 0.9 gram sodium bromide. High quality development is obtained.

Example 5

The procedure according to Example 3 is followed except that the developer contains the dissolved residues from 1.16 grams diaminopropanol tetraacetic acid and the replenisher contains the dissolved residues from 1.3 grams of the same compound plus 0.9 gram sodium bromide. Consistant, high-quality development is obtained at a replenishment rate of 242 ml. per square foot of picture area processed.

Example 6

A two-component developer replenisher is prepared containing Parts A and B as follows:

Part A

An acidic aqueous developing agent solution is prepared by adding 0.3 grams sodium sulphite (0.19 gram sulphite) to 8 grams distilled water and stirring until the sodium sulphite is completely dissolved; then dissolving 6.4 grams 4 - amino - N - ethyl - N - [β - methanesulphonamidoethyl] - m - toluidine sesquisulphate monohydrate in the sulphite solution; adding to the resultant acidic solution 6.6 grams benzyl alcohol with vigorous stirring to form cloudy slurry; and then gradually adding 7.8 grams of ethylene glycol to the slurry to form a clear solution. This solution exhibits excellent storage stability.

Part B

A buffered aqueous alkaline solution is prepared by dissolving 3.4 grams of sodium hydroxide and 23.3 grams of potassium hydroxide in 42 grams water; gradually adding to this solution 29 grams boric acid, 1.7 grams sodium sulphite, 1.3 grams diamino propanol tetraacetic acid, and 0.8 gram sodium bromide and adjusting the pH to 10.75±0.05 at 27°C. by the addition of small amounts of potassium hydroxide. The solution is stable for long periods of time at varying temperatures.

Example 7

A developer replenisher is prepared by slowly adding the solution from Example 6A to about 800 ml. of water and stirring to assure complete dissolution; slowly adding the solution from Example 6B with stirring; and adding sufficient water to bring the total volume to one litre.

Example 8

The procedure according to Example 3 is followed except that the solution from Example 7 is utilized in place of the replenisher from Example 2. Satisfactory results are achieved with a developer replenisher rate of 243 ml. per square foot of picture area processed.

Example 9

The procedure according to Example 8 is followed except that the developer of Example 3 also contains the dissolved residues from 1.2 grams of diamino propanol tetraacetic acid. Excellent results are achieved with a developer replenisher rate of 243 ml. per square foot of picture area processed (160 ml. per square foot of film processed).

Example 10

A developer replenisher is prepared containing the dissolved residues from 7 grams benzyl alcohol, 29 grams boric acid, 3.4 grams sodium hydroxide, 23.5 grams potassium hydroxide, 2.1 grams sodium sulphite, 1.3 grams diaminopropanol tetraacetic acid, 0.4 gram sodium bromide, and 7.9 grams 4 - amino - N - ethyl - N - [β - methane - sulphonamidoethyl] - m - toluidine sesquisulphate monohydrate per litre of aqueous solution. The resultant solution has a pH of 10.78 at 27°C. and shows no signs of crystallization or precipitation at temperatures ranging as low as 10°C.

Example 11

The procedure according to Example 3 is

followed except that the solution from Example 10 is utilized in place of the solution from Example 2 and the developer which is replenished contains 1.2 grams diaminopropanol tetraacetic acid and 5 mg. potassium iodide. Satisfactory results are achieved at a replenishment rate of 121 ml. per square foot of picture area processed (80 ml. per square foot of processed film).

Example 12

The procedure according to Example 11 is followed except that a developer replenisher containing 7.7 grams benzyl alcohol, 8 grams ethylene glycol, 1.3 grams diaminopropanol tetraacetic acid, 29 grams boric acid, 3.4 grams sodium hydroxide, 23.5 grams potassium hydroxide, 2.2 grams sodium sulphite, no bromide, and 9.4 grams 4 - amino - N - ethyl - N - [β - methanesulphonamido - ethyl] - m - toluidine sesquisulphate monohydrate per litre of solution is used in place of the replenisher from Example 10. Satisfactory results are achieved at a developer replenishment rate of 77 ml. per square foot of picture area processed (52 ml. per square foot of processed film).

Example 13

The procedure according to Example 11 is followed except that a replenisher solution is prepared from a two-component replenisher kit by procedures outlined in Example 7. Part A of the replenisher kit is identical to Example 6, Part A. Part B of the replenisher contains the same ingredients but 11 grams more more water than Example 6, Part B. The replenisher functions extremely effectively at a replenishment rate of 243 ml. per square foot of picture area processed.

WHAT WE CLAIM IS:—

1. A method of processing photographic multilayer, silver halide, incorporated coupler, negative colour films wherein a developer replenisher is employed which contains a p-phenylenediamine developing agent, benzyl alcohol and sulphite ions and has a pH of at least 10.5 at 24°C. characterised in that the developer replenisher contains potassium and sodium ions in a potassium/sodium ion weight ratio of at least 2.5/1.

2. A method as claimed in Claim 1 in which the developer replenisher contains a buffering system which maintains a pH of from 10.5 to 11 at 24°C.

3. A method as claimed in claim 1 or 2 in which the developer replenisher contains no more than 0.80 gram bromide ions per litre.

4. A method as claimed in any of claims 1—3 in which the developer replenisher contains a sequestering agent.

5. A method as claimed in any of Claims 1—4 in which the developer solution contains the same components as the developer replenisher including potassium and sodium ions in a potassium/sodium ion weight ratio of at least 2.5/1.

6. A method of processing photographic multilayer, silver halide, incorporated coupler, negative colour films according to Claim 1 substantially as described herein with reference to the Examples.

7. A developer replenisher solution having a pH of at least 10.5 at 24°C. and containing potassium and sodium ions, a p-phenylenediamine developing agent, benzyl alcohol and sulphite ions characterised in that potassium and sodium ions are present in a potassium-sodium ion weight ration of at least 2.5/1.

8. A replenisher solution as claimed in Claim 7 which contains a buffering system which maintains a pH of from 10.5 to 11 at 25°C.

9. A replenisher solution as claimed in Claim 8 in which the buffering system is a boric acid-borate buffer.

10. A replenisher solution as claimed in any of Claims 7—9 which contains from 4 to 8 grams benzyl alcohol, from 3 to 5 grams p-phenylene diamine developing agent (as free amine), from 1.25 to 1.55 grams sulphite, from 19 to 28.5 grams borate per litre of solution.

11. A replenisher solution as claimed in any of Claims 7—10 which contains no more than 0.80 gram bromide ions per litre of solution.

12. A replenisher solution as claimed in any of Claims 7—11 which contains a sequestering agent.

13. A replenisher solution as claimed in Claim 12 which contains from 0.5 to 2 grams sequestering agent per litre of solution.

14. A developer replenisher solution according to Claim 7 substantially as described herein with reference to the Examples.

15. A developer replenisher kit comprising at least two aqueous solutions one of which contains a buffered solution having a pH of at least 10.5 at 24°C. and containing sulphite, another solution containing the developing agent and having a pH of less than 6 at 24°C, which solutions when mixed together and with water provide a developer replenisher solution according to any of claims 7—14.

16. A developer replenisher kit as claimed in Claim 15. in which the developing agent solution also contains sulphite.

17. A developer replenisher kit as claimed in Claim 16 in which the sulphite is present in the developing agent solution in a developing agent (as free amine)/sulphite mole ratio of from 1/0.08 to 1/1.5.

18. A developer replenisher kit as claimed in Claim 16 or 17 in which the sulphite present in the developing agent solution is in a developing agent (as free amine)/sulphite mole ratio of from 1/0.15 to 1/0.5, the

buffered solution containing sufficient sulphite to provide a total developing agent (as free amine)/sulphite mole ratio of at least 1/1.6.

19. A developer replenisher kit as claimed in any of Claims 15—18 in which the developing agent solution contains benzyl alcohol and a liquid glycol having a carbon/oxygen ratio of from 0.75/1 to 1.5/1 and a molecular weight of from 62 to 150, the water/benzyl alcohol weight ratio being from 1/6 to 5/1.

20. A developer replenisher kit as claimed in any of Claims 15—19 in which the buffered solution contains potassium and sodium ions in a potassium/sodium ion weight ratio of from 5.4/1 to 10/1.

21. A developer replenisher kit according to Claim 15 substantially as described herein with reference to the Examples.

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